Paper

Quick Observation of Photoelectron Emission Microscopy with Focused Soft X-rays using Poly-capillary Lens

Norie Hirao,* Yuji Baba, Tetsuhiro Sekiguchi and Iwao Shimoyama

Japan Atomic Energy Agency, Tokai-mura, Naka-gun, Ibaraki, 319-1195, Japan

*hirao.norie@jaea.go.jp

In order to study dynamic phenomena in a microscopic region of solid surfaces, it is important to observe element, chemical-state, and molecular-orientation mappings at nanometer scale in a short time. In the previous study, we have developed a photoelectron emission microscopy (PEEM) system combined with soft X-rays from synchrotron light source, and demonstrated that the method can be applied to the observation on chemical-state mapping of silicon compounds at nanometer scale [1]. In the present work, in order to apply this method to the observation of fast phenomena, we explored the focusing of soft X-ray (1.8 – 4 keV) using a poly-capillary lens, and examined the minimum measuring time by PEEM. By adjusting the poly-capillary lens, the brightness of the measuring spot by PEEM became about 55 times higher than that without the lens. Consequently, we can take a PEEM image of a bulk sample in 10 msec. The measuring times for elemental mapping and chemical-state mapping were also examined by scanning the energy of X-ray. As a result, the typical minimum measuring times were in the order of 10 sec for elemental mapping and one minute for chemical-state mapping. It is demonstrated that the method will be applicable to the real-time observation of time-dependent phenomena in the order from msec to sec at nanometer scale.

1. Introduction

Photoelectron emission microscopy (PEEM) is recently developed powerful tool to observe surface of materials at nanometer scale. Among various types of PEEMs, an imaging-type PEEM where total photoelectrons are expanded by electrostatic lenses is suitable for the measurement of fast phenomena because of its high detection efficiency [2,3]. In the previous study, we have developed a PEEM system combined with soft X-rays from synchrotron light source, and demonstrated that the method can be applied to the observation of chemical-state mapping of silicon compounds [1] and molecular-orientation mapping of organic thin films [4] at nanometer scale.

In order to observe dynamic phenomena such as surface chemical reactions and surface diffusion, it is necessary to take a PEEM image in shorter time. For this purpose, it is required to focus the X-rays on a small spot where PEEM images are taken.

X-ray beams are generally focused using various types of X-ray optics such as a bent mirror [5,6], a zone plate [7] and refractive lenses [8-10]. Besides these X-ray focusing optics, a poly-capillary lens is recently developed simple focusing tool for X-ray, proposed by Kumakhov [11]. So far, poly-capillary lenses have been applied to the focusing of hard X-ray [12-14], while it has scarcely been used in soft X-ray and vacuum ultraviolet light.

A poly-capillary lens has an advantage over the other focusing tools, because the focusing position never changes even when the X-ray energy is changed [15]. A poly-capillary lens is a straight tube that can be put in front of a sample. Therefore, there is another advantage that we can easily exchange between focused and unfocused beams by simply moving the tube up and down.

In this paper, we present the results for the focusing test of synchrotron soft X-rays using a poly-capillary lens, and reveal the enhancement of the photon flux in a microscopic area. As a typical example for quick observation of element-mapping at nano-scale, we will

Journal of Surface Analysis Vol.17, No.3 (2011) pp.227-231

N. Hirao et al. Quick Observation of Photoelectron Emission Microscopy with Focused Soft X-rays using Poly-capillary …

demonstrate the measuring time for patterned Si-Au sample. The measuring time for chemical-state mapping is also presented for Si-SiO$_2$ system.

2. Experimental

All the experiments were performed at the end station of the beamline 27A (BL-27A) of the Photon Factory of the High Energy Accelerator Research Organization (KEK-PF), Tsukuba, Japan. Fig. 1 shows an outline of the experimental setup. The synchrotron radiation (SR) beam was generated from the bending magnet and it was linearly polarized in the horizontal direction. Double-crystals of InSb (111) were used as a monochromator. The total energy resolutions of this monochromator were 0.85 eV at 1.84 keV (Si K-edge), and 1.37 eV at 2.75 keV (Au M_3-edge).

A poly-capillary lens is recently developed simple focusing tool for X-ray, proposed by Kumakhov [11]. The poly-capillary consists of a bundle of thousands or millions of glass capillaries, and the X-rays in the capillaries are totally reflected from the internal surface of the tubes. Generally, a poly-capillary lens is used in X-ray tube, that is, a point source [16,17]. Therefore, a full poly-capillary lens has two parabolic parts. The X-rays from point source become parallel beam by the front part, and then they are focused on a small point by the rear part [18]. In this work, parallel X-ray beam from synchrotron light source is used. Consequently, a half poly-capillary lens (the rear part of a full poly-capillary lens) was utilized. The most excellent property of a poly-capillary lens is that the focusing point never changes with the photon energy, so it is suitable for the present experiment, in which the PEEM images are measured by changing X-ray energy.

The PEEM system used was an Elmitec Co. Model PEEMSPECTOR. The synchrotron beam was irradiated at 60 degrees from the surface normal. The take-off direction of electrons was the surface normal. The total photoelectrons emitted from the sample surface were accelerated at 15 kV, and magnified using electrostatic lenses. The electrons were multiplied by a micro-channel plate (MCP) and focused on a YAG fluorescence screen, and then taken into a CCD camera. The spatial resolution of the PEEM system was estimated to be 42 nm.

It should be noted that the intensity of total photoelectrons emitted from the surface is proportional to the absorption of X-ray in the surface layer. So if we change the energy of X-ray around the absorption edge, we can observe microscopic image depending on the yield of X-ray absorption at the corresponding energy.

As a sample for the element-mapping, a micro-pattern made of silicon and gold was used. The sample was prepared in the following procedure. First, a thin film of gold was deposited on a clean surface of Si (001). Then a rectangular mask of 25 μm periodicity (9 μm blank and 16 μm space) was put on the surface, and it was sputtered by Ar$^+$ ions. Then the mask was taken out.

As a sample for the chemical-state mapping, a micro-pattern made of silicon and silicon dioxide was used. The sample was prepared in the following procedure. Five keV O$_2^+$ ions were implanted in a Si (001) wafer using a mask of 12.5 μm periodicity (5.0 μm blank and 7.5 μm space). After ion implantation, the mask was taken off in the atmosphere. In the previous study, it was confirmed that the SiO$_2$ is formed when O$_2^+$ ions are implanted in a silicon wafer [19].

3. Results and Discussion

Fig.2 displays PEEM images for Au-Si micro-pattern excited by 3 keV photons. The bright areas in the image are due to gold, while dark areas originate from silicon. The image (a) was measured for 60 sec without poly-capillary lens. On the other hand, the images (b), (c) and (d) were taken for 1 sec, 100 msec and 10 msec, respectively, with the poly-capillary lens. As measuring time becomes shorter, the image becomes dark and noises increase. Nevertheless, the pattern can be still clearly identified in image (d). Therefore, it is revealed that 10 msec is enough to take a PEEM image for bulk materials like present Au-Si pattern.
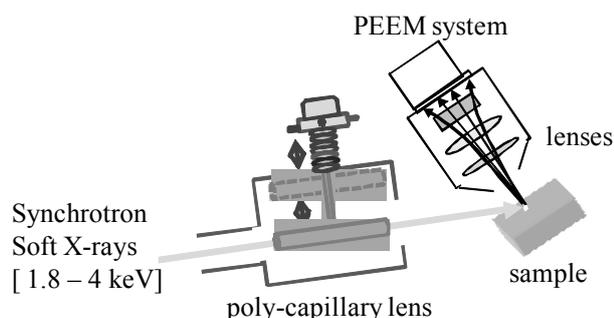

Fig.1. Schematic illustration of the experimental setup.

Journal of Surface Analysis Vol.17, No.3 (2011) pp.227-231

N. Hirao et al. Quick Observation of Photoelectron Emission Microscopy with Focused Soft X-rays using Poly-capillary …
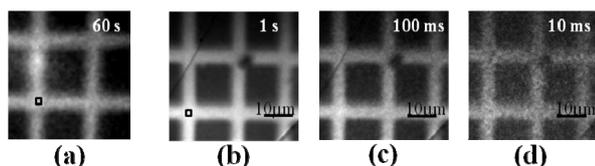
(a) **(b)** **(c)** **(d)**

Fig.2 PEEM images of Si-Au micro-pattern excited by 3keV photons. Image (a) was taken without poly-capillary lens, and images (b), (c) and (d) were taken with poly-capillary lens. The measuring time is shown in each image. Black squares shown in images (a) and (b) are regions where brightnesses were compared in Table 1.

Table 1 Brightness of black-square regions in images (a) and (b) of Fig. 1 at four different photon energies. I_0 is dark count without X-rays. I_1 and I_2 are brightnesses without and with poly-capillary lens, respectively. R is intensity ratio which is defined as R = $(I_2-I_0)/(I_1-I_0)$.

Photon Energy [keV]	1.8	2.0	3.0	4.0
(I_1-I_0)[cps]	172	35	62	51
(I_2-I_0)[cps]	206	526	3386	498
R	1.2	15	55	9.7

Next, we compared the photon fluxes with and without poly-capillary lens. Table 1 summarizes the brightness of the black square regions in images (a) and (b) of Fig.2 at four different X-ray energies. R is the intensity ratio which is defined as R= $(I_2-I_0)/(I_1-I_0)$ where I_0 is dark count without X-rays. I_1 and I_2 are brightnesses without and with poly-capillary lens, respectively. A remarkable enhancement of the brightness is observed at 3 keV, where the R value is about 55.

The reflectivity of X-ray by glass increases from 2keV to 4keV, so the R value should be maximum at 4keV. The photon energy dependence of R value in Table 1 is due to the decrease in SR-beam flux passing through the poly-capillary lens by the change of SR-beam position with photon energy. So, the measuring time of PEEM is appreciably shortened.

In order to know how fast we can observe the element mapping, the photon energy was scanned around the Si and Au absorption edges, and PEEM images were taken. Fig.3 (a) shows the PEEM image excited by photons at 2752 eV. In order to identify the element in each domain of Fig.3 (a), we have measured the photon-energy dependences of the brightnesses of the spots A and B of Fig.3 (a). In Fig.3 (b) and (c), the brightnesses of the spots A and B are plotted as filled and open circles, respectively. Fig.3 (b) shows brightness plot around the Au M_3-edge. The

solid line exhibits the X-ray absorption fine structure (XAFS) spectrum of gold, which was measured by total electron yield. The shape of the plots of filled circles is similar to XAFS spectrum for gold. Thus, it is easily identified that the spot A consists of gold. Fig.3 (c) displays brightness plot around the Si K-edge. The solid line shows the XAFS spectrum of elemental silicon. Thus, it is easily identified that the spot B consists of
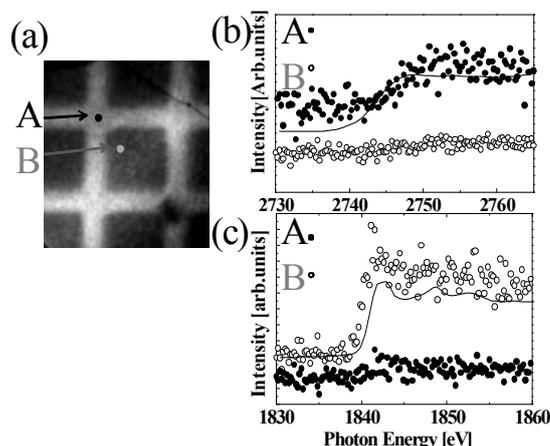

Fig. 3 (a) PEEM image of Si-Au micro-pattern excited by 2752eV photons using poly-capillary lens. (b) Photon energy dependences of the brightnesses of the spots A and B in the image (a) around Au M_3-edge. The measuring time of one point is 1 sec. Solid line shows the XAFS spectrum of gold. (c) Same as (b) but around Si K-edge. Solid line shows the XAFS spectrum of silicon.

elemental silicon. So, we can obtain the XAFS spectra in all domains in the PEEM image. For XAFS spectra in all domains, the measuring time depends on how clear spectra we want to obtain, but as shown in Fig.3 (b) and (c), a typical measuring time for XAFS spectra with good statistics is a few minutes. And the minimum measuring time is in the order of 10 sec. Thus, the method can be applied to the quick mapping of elements at nanometer scale.

As an example of a quick chemical-state mapping, the method was applied to the observation of the Si-SiO$_2$ micro-pattern. Fig.4 (a) shows the PEEM image of the Si-SiO$_2$ micro-pattern. The photon energy of the image is just corresponding to the Si 1s→σ* resonance peak in the XAFS spectrum for SiO$_2$ (hν=1847eV) [20]. In order to identify the valence states of silicon in each domain of Fig.4 (a), the brightnesses of the spots A and B in the image (a) are plotted as filled and open circles, respectively. Fig.4 (b) and (c) show the brightness plots around the Si K-edge. The measuring times of one point for (b) and (c) are 10 sec and 1sec, respectively. For a comparison, the XAFS spectra of elemental
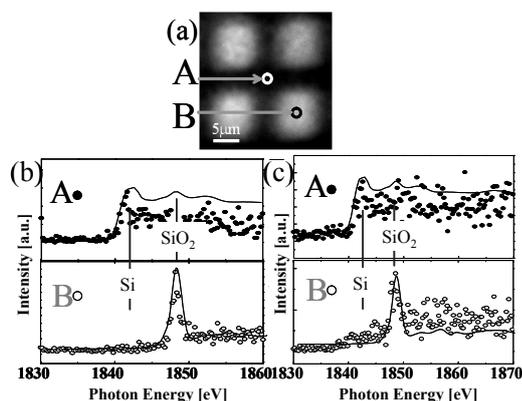
Journal of Surface Analysis Vol.17, No.3 (2011) pp.227-231

N. Hirao et al. Quick Observation of Photoelectron Emission Microscopy with Focused Soft X-rays using Poly-capillary …

Fig.4 (a) PEEM image of Si/SiO$_2$ micro-pattern excited by 1847eV photons using poly-capillary lens. (b) Photon energy dependences of the brightnesses of spots A and B in the image (a). The measuring time of one point is 10 sec. Black line shows the XAFS spectra for Si and SiO$_2$. (c) Same as (b) but the measuring time of one point is 1sec.

Si and SiO$_2$ are also shown as solid lines. The curves of the open and filled circles are similar to the XAFS spectra for SiO$_2$ and Si, respectively. So it was elucidated that the spots A and B surely correspond to Si and SiO$_2$, respectively. As to the measuring time for chemical-state mapping, Fig.4 (c) shows that one minute is enough to identify the valence states of silicon.

Since the changes in the brightness in PEEM images are due to the X-ray absorption intensity of the respective chemical states, we could identify the valence state of silicon at every pixel in the PEEM image in a similar way. Thus, the method can be applied to the quick mapping of electronic structures and chemical-states.

Consequently, we can obtain the element and chemical-state mapping in the order of 10 sec and 1 minute, respectivel, using poly-capillary lens. XAFS gives the information about not only elements and chemical states but also electronic structures, molecular orientations and magnetic structures [21-24], this method will highlight the further applications for the real-time measurements of dynamic phenomena such as surface chemical reactions and surface diffusion. Further experiments about fast observations at real-time for surface diffusion of silicon compounds and organic thin films [25] are now in progress.

4. Acknowledgements

5. References

[1] N. Hirao, Y. Baba, T. Sekiguchi, I. Shimoyama and M. Honda, *Anal. Sci.* **26,** 835 (2009).

[2] W. Telieps and E. Bauer, *Ultramicroscopy* **17**, 57 (1985).

[3] H.H. Rotermund, W. Engel, M.E. Kordesch and G. Ertl, *Nature* **343,** 355 (1990).

[4] Y. Baba, T. Sekiguchi, I. Shimoyama, M. Honda, N. Hirao, A. Narita and J. Deng, *Surf. Sci.* **603**, 2612 (2009).

[5] H. Mimura, S. Matsuyama, H. Yumoto, H. Hara, K. Yamamura, Y. Sano, M. Shibahara, K, Endo, Y. Mori, Y. Nishino, K. Tamasaku, M. Yabashi, T. Ishikawa and K. Yamauchi, *Jpn.J.Appl .Phys.* **44**, 539 (2005).

[6] H. Takano, S. Aoki, M. Kumegawa, N. Watanabe, T. Ohhigashi, T. Aota, K, Yamamoto, H, Yokosuka, R. Tanoue, Y. Tsujita and M. Ando, *Rev.Sci.Instrum.* **73**, 2629 (2002).

[7] Y. Suzuki, A. Takeuchi, H. Takano, T. Ohigashi and H. Takenaka, *Jpn. J. Appl. Phys.* **40**, 1508 (2001).

[8] C. Huang, B. Mu, Z. Wang, L. Chen and Y. I. Dudchik, *Nucl. Instrum. Meth. Phys. Res. B* **602**, 446 (2009).

[9] P. Elleaume, B. Filseth, Th. Kolocke, V. Kohn, B. Lengeler, I. Snigirev, A. Souvorov and J. Tummler, *Proc.SPIE* **3151A**, 164 (1997).

[10] A. Snigirev, V. Kohn, I. Snigireva, A. Souvorov and B. Lengeler, *Appl.Opt.* **37**, 653 (1998).

[11] M. A. Kumakhov, *X-ray Spectrom.* **29**, 343 (2000).

[12] F. A. Hofmann, C. A. Freinberg-Trufas, S. M. Owens, S. D. Padiyar and C. A. Macdonald, *Nucl. Instrum. Meth. Phys. Rev. B* **133**, 145 (1997).

[13] A. Rindby, P. Engstrom, K. Janssens and J. Osan, *Nucl. Instrum. Meth. Phys. Rev. B* **124**, 591(1997).

[14] K. Proost, L. Vincze, K. Janssens, N. Gao, E. Bulska, M. Schreiner and G. Falkenberg, *X-ray Spectrom.* **32**, 215 (2003).

[15] T. Sun, Z. Liu, B. He, S. Wei, Y. Xie, T. Liu, T. Hu and X. Ding, *Nucl. Instrum. Meth. Phys. Rev. A* **574**, 285 (2007).

[16] T. Emoto, Y. Sato, Y. Konishi, X. Ding and K. Tsuji, *Spectrochimica Acta, Part B* **59**, 1291 (2004).

[17] K. Janssens, F. Adams and A. Rindby, in *Microscopic X-Ray Fluorescence Analysis*, 2nd Edn ed. by A. Rindby, F. Adams and P.

Journal of Surface Analysis Vol.17, No.3 (2011) pp.227-231

N. Hirao et al. Quick Observation of Photoelectron Emission Microscopy with Focused Soft X-rays using Poly-capillary …

Engström, Chapt. 3, pp. 77-87 JohnWiley, Chichester (1990).

[18] A. Bjeoumikhov, M. Erko, S. Bjeoumikhova, A. Erko, I. Snigireva, A. Snigirev, T. Wolff, I. Mantouvalou, W. Malzer and B. Kanngieβer, *Nucl. Instrum. Meth. Phys. Rev.*, *A* **587**, 458 (2008).

[19] Y. Baba, H. Yamamoto and T.A. Sasaki, *Phys. Rev. B*, **48**, 10972 (1993).

[20] Y. Baba, *Low. Temp. Phys.* **29**, 228 (2003).

[21] F.U. Hillebrecht, H. Ohldag, N.B. Weber, C. Bethke, U. Mick, M. Weiss and J. Bahrdt, *Phys. Rev. Lett.*, **86**, 3419 (2001).

[22] H. Ohldag, T.J. Regan, J. Stöhr, A. Scholl, F. Nolting, J. Lüning, C. Stamm, S. Anders and R.L. White, *Phys.*, *Rev. Lett.* **87**, 247201 (2001).

[23] T. Kinoshita, T. Wakita, H.-L. Sun, T. Tohyama, A. Harasawa, H. Kiwata, F.U. Hillebrecht, K. Ono, T. Matsushima, M. Oshima, N. Ueno and T. Okuda, *J. Phys. Soc. Jpn.* **73**, 2932 (2004).

[24] T. Okuda, T. Matsushima, T. Wakita, A. Harasawa, T. Kinoshita, H. Kiwata, K. Ono, T. Kihara, M. Oshima and A. Yokoo, *Jpn. J. Appl. Phys*. **43**, 4179 (2004).

[25] Y. Baba, T. Sekiguchi, I. Shimoyama and N. Hirao, *J. Surf Anal.* **17**, 333 (2011).